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Historical perspective

Surface modification using TEMPO and its derivatives

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ABSTRACT

This article provides an overview of the methods for surface modification based on the use of stable radicals: 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) and its derivatives.

Two approaches are discussed. The first relies on the immobilization of TEMPO moieties on the surface of various materials including silicon wafers, silica particles, organic polymers as well as diverse nanomaterials. Applications of such materials with spin labeled surface/interface, in (electro)catalysis, synthesis of novel hybrid nanostructures and nanocomposites as well as in designing of organic magnets and novel energy storage devices are also included in the discussion.

The second approach utilizes TEMPO and its derivatives for the grafting of polymer chains and polymer brushes formation on flat and nanostructure surfaces *via* Nitroxide Mediated Radical Polymerization (NMRP). The influence of such polymer modification on surface/interface physicochemical properties is also presented.

Contents

1. Introduction

The design and fabrication of modified surfaces is a pivotal research issue in modern materials science. Appropriate surface modification is an effective approach in the preparation of new tailor-made materials for catalytic, protective, biomedical, sensory and many other purposes.

TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) is undoubtedly the most prominent compound among stable nitroxide radicals. The high stability of TEMPO and its derivatives mainly results from the following phenomena: (1) the delocalization of one unpaired electron over the nitrogen oxygen bond, (2) an inability to disproportionate to the

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corresponding nitrone and hydroxylamine because of a lack of α hydrogen atoms, and (3) an inability to recombine with itself because of steric hindrance of methyl groups [1]. This persistent, cyclic nitroxide radical and its derivatives are extensively used as oxidation catalysts for organic synthesis [2–6], mediators for controlled polymerization [7], spin probes for biochemical research [8], magnetic resonance imaging (MRI) contrast agents [9], dynamic nuclear polarization (DNP) agents for NMR spectroscopy [10], building blocks for the preparation of organic magnets [1], and antioxidants in biological systems [11].

For detailed information on structure, properties and synthesis of TEMPO and its derivatives the reader is referred to recently published book and reviews on nitroxides [1,4,5].

Although TEMPO and many of its derivatives are known from the 1960s; however the first reports on their use in surface modification processes appeared just twenty years ago. Among the numerous TEMPO derivatives the ones carrying the substituents at position 4 in the piperidine ring (Fig. 1) are particularly relevant because of their application in surface modification processes. It is worth mentioning that some of them also find important industrial exploitations. Applications of TEMPO and its derivatives as highly selective oxidation catalysts for the production of pharmaceuticals, flavors, fragrances, agrochemicals and a variety of other specialty chemicals have been elegantly reviewed by Ciriminna and Pagliaro [12].

In fact, TEMPO is a strong inhibitor of aerobic oxidation, but it can be easily and reversibly oxidized to the corresponding oxoammonium cation (**7**) (Fig. 2), which can be used as a relatively strong oxidizing agent for various alcohols and sugars [2,3]. As a result of two-electron reduction of oxoammonium species under the influence of a reducing agent, *e.g.* an alcohol or reducing sugar, a hydroxylamine (**8**) is formed. Simultaneously, alcohols are converted to carbonyl compounds, while reducing sugars are transformed to glucoronates.

The application of appropriate co-oxidant systems capable of reoxidizing hydroxylamine to nitroxide and subsequently to oxoammonium ion provides the possibility of using TEMPO and its derivatives as oxidation catalysts. However, considering the high cost of TEMPO (80–100$/kg) [12], even if catalytic quantities are used, its efficient recycling is highly desirable, particularly when the process is performed on a large scale. The separation methods conventionally used for this purpose (*e.g.* azeotropic distillation, chromatography, liquid-liquid extraction) are time-consuming, costly and difficult to scale-up. Obviously, the immobilization of catalyst on the surface enables its easy separation and recycling; therefore, this is highly preferred not only from an economic, but also from an environmental point of view. Further, in the pharmaceutical industry perfect separation of the catalyst is strictly required due to the necessity for high purity products. Consequently, considerable efforts have been made to develop TEMPO modified surfaces for applications in catalysis. For these applications, nitroxides must be grafted onto the surface *via* a non-radical fragment of the molecule through the appropriate linker (Y), to ensure availability of >NO• groups (Fig. 3a).

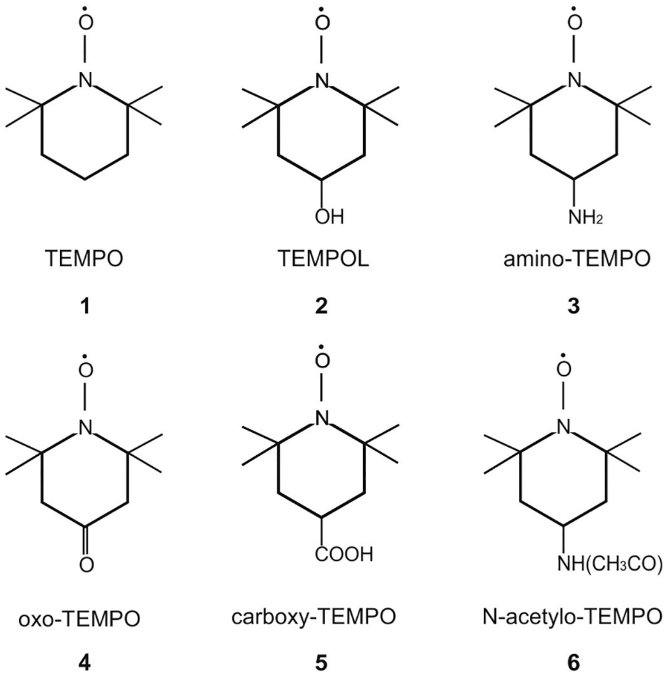

Fig. 1. The structure of TEMPO and its selected derivatives.

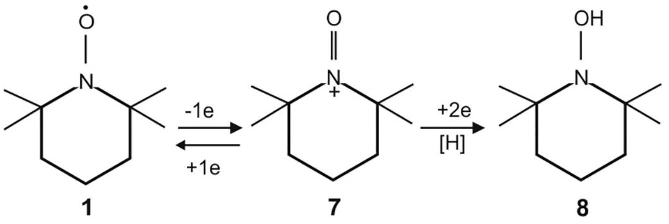

Fig. 2. Reversible oxidation of TEMPO and two-electron reduction of oxoammonium ion.

The first part of this review focuses on the immobilization of compounds containing a TEMPO moiety onto the surface and the utility of the obtained materials as reusable catalysts in oxidation reactions, redox-active materials in organic batteries, antibacterial agents, novel magnetic materials and others. In this section of the review, the immobilization of TEMPO moieties onto a flat inorganic (silica, metal, metal oxides) and organic (polymer) surfaces, as well as on nanostructures, such as nanoparticles, nanotubes, fullerenes, an graphene sheets, has been highlighted.

The following section will discuss surface modification processes consisting of polymer grafting onto surfaces by using TEMPO and its derivatives as mediators in controlled radical polymerization. In this case TEMPO and its derivatives are grafted to the surface *via* >NO• groups and form appropriate alkoxyamine/macroalkoxyamine molecule connected with the surface by appropriate linker (Y) (Fig. 3b). Such surfaces have not radical character, however, under the influence of appropriate thermal/photochemical stimulus a bond between TEMPO and alkyl group/polymer chain can undergo homolysis. Then, the radicals attached to the surface can propagate resulting in the growth of (co)polymer chains. Simultaneously, the presence of TEMPO enables the formation of polymer brushes with well-defined structure, controlled molecular weight and narrow polydispersity.

Other nitroxides can also be used for surface modification [13]; however, as this review focuses on the application of TEMPO and its derivatives, their utilization will not be discussed here.

2. Immobilization of TEMPO onto inorganic surfaces

The immobilization of a TEMPO moieties onto inorganic supports (*e.g.* silica, metals, metal oxides) has been actively studied over the past two decades especially for catalytic applications.

As mentioned earlier, TEMPO and its derivatives can be successfully applied as catalysts for the oxidation of alcohols, diols and sugars in homogeneous systems. Typically, this reaction is performed with small amounts of TEMPO (*ca.* 1 mol%) by using a stoichiometric quantity of terminal oxidant (co-oxidant). The co-oxidant regenerates oxoammonium ion (**7**) from hydroxylamine (**8**) (Fig. 4).

The following systems are most often used as terminal oxidants ([Ox]) for oxoammonium ion reconversion: hypochlorine in combination with bromides (Anelli protocol), bis(acetoxyiodo)benzene $PhI(OAc)_2$ (Margarita protocol), *meta*-chloroperbenzoic acid (m-CPBA), *N*-chlorosuccinimide, oxone, and oxygen in combination with CuCl or ruthenium complexes [2–5]. Notably, electrochemical regeneration of

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